partitions of the pyramid are determined in terms of those of the r-gon and r-ace.

Thus the entire first class of r-gonous x-edra is enumerated, without descending to any classification of polyedra according to the rank of their faces and summits. The enumeration of the second and higher classes will require such classification, which will introduce so vast a complexity as to render the further prosecution of the theory of the polyedra, in the opinion of the author, practically impossible by any method deserving the name of scientific generality.

III. "Researches on the Cinchona Alkaloids." By W. Bird Herapath, M.D. Lond., F.R.S.E. Communicated by Prof. Stokes, Sec. R.S. Received June 19, 1857.

(Abstract.)

Part I.—Critical examination of the ordinary methods employed for the discrimination of the Cinchona Alkaloids, viz. Quinine, Quinidin, and Quinicine and Cinchonine, Cinchonidin and Cinchonicine; together with the optical and chemical characters of their Iodo-Sulphates, upon which new methods are founded.

In consequence of the gradually increasing scarcity of the *cortex cinchonæ calysayæ* and its chief product quinine, many other barks have been introduced into commerce, which furnish alkaloids having a strong general resemblance in the physical characters of those preparations of them more commonly employed in medicine, but differing widely in medicinal properties and commercial values.

In order to prevent fraudulent adulterations, it has long been highly desirable to have some ready methods of detecting admixtures of these alkaloids and their salts. The author having discovered several optical salts of these vegetable alkaloids, proposes to make their well-marked optical characters the means of such detection, and in the second part of this paper has fully developed his views upon this ready method of analysis, whilst in the present part he has passed under review the various existing tests for the different cinchona alkaloids, and the results of his investigations may be enumerated under the following conclusions:—

The following different methods of detecting the various cinchona alkaloids have been proposed :—

To Bouchardat and Pasteur we are indebted for the use of polarized light as a means of discriminating these alkaloids by the rotatory power which they exercise upon its plane.

Liebig employs the difference of their solubility in ether for the same purpose.

Almost all the other tests proposed have for their object only the discovery of quinine.

Professor Stokes employs fluorescence, combined with the peculiar reaction, in respect to this phenomenon, of hydrochloric acid, alkaline chlorides, &c. Brandes, the green reaction produced by the successive addition of chlorine and ammonia, whilst Vogel has modified this latter test in several ways.

Pelletier has employed the agency of a stream of chlorine gas, and Marchand uses nascent oxygen, obtained from puce-coloured oxide of lead and sulphuric acid for the discovery of quinine.

Leers first proposed a combination of Liebig's ether test, with that of Brandes's chlorine and ammonia reaction, as a means of establishing the purity of cinchonidin (miscalled by him quinidin, in common with all German chemists).

De Vry has advised the employment of hydriodic acid or iodide of potassium in order to discover the quinidin of Pasteur.

Van Heijningen depends on oxalate of ammonia to discriminate quinine from quinidin.

All these different tests the author has examined most critically, and, as far as it is possible to do so, determined the absolute numerical value of each method experimentally with the following results :—

He first explains MM. Bouchardat and Pasteur's researches on these remarkable alkaloids, from which it appeared that quinine and cinchonidin are powerfully lævogyrate, quinidin and cinchonine pre-eminently dextrogyrate, and that quinicine and cinchonicine are only slightly dextrogyrate upon plane-polarized light. These eminent experimenters determined also with accuracy the amount of these molecular rotations for each alkaloid. Yet the expensive nature of the apparatus, the complex formula requisite to reduce the observed amount of angular rotation to the normal molecular standard, and

the many interfering actions necessary to be guarded against, effectually prevented this from ever becoming a process for general adoption, either among chemists or manufacturers.

Another method of recognizing the presence of quinine is founded on the optical phenomena of fluorescence, which have been investigated by Professor Stokes. Whilst endeavouring to turn this process to account in the quantitative estimation of quinine by means of excessive dilution, and marking the points at which the various phenomena of "epipolism," "fluorescence," and "internal dispersion" vanish, the author arrived at the following extraordinary results; premising that he employs the term "internal dispersion" to mean the positive, "fluorescence" the comparative, and "epipolism" the superlative degrees of the same optical power:—

I. Solutions containing 1 grain in 35,000 of either quinine or quinidin of Pasteur, exhibit epipolism and fluorescence; solutions with 1 grain in somewhat less than 140,000 grains of water are still fluorescent, with slight internal dispersion.

When diluted with from 3 to 10 gallons of water, these alkaloids continue to exhibit internal dispersion.

Solutions of quinicine are only slightly epipolic, and if the change has been perfect, scarcely at all fluorescent, but nevertheless strongly absorptive of rays of high refrangibility.

Cinchonidin also exhibits optical phenomena, but in a much slighter degree; about $\frac{1}{100}$th part of that of either quinine or quinidin.

Cinchonine is also fluorescent about $\frac{1}{120}$th part of the same alkaloids.

II. That on mixing fluorescent solutions of quinine, quinidin, or other cinchona alkaloid with the soluble chlorides, although all traces of optical phenomena are lost to the eye, yet the media still possess powerfully absorbent powers on the rays of high refrangibility, and, if sufficiently concentrated, are wholly opaque to them, without exhibiting any of the phenomena of dispersion, and greatly impede chemical action.

This was proved by three methods of observation:—

1st. By introducing vessels containing fluorescent solutions of quinine into other vessels filled with non-fluorescent solutions of the alkaloids, produced by previous admixture with chloride of ammonium, when all optical phenomena disappeared from the inner vessel.

2ndly. By surrounding fluorescent specimens of fluor-spar with these prepared solutions of the alkaloids, when the blue colour in the spar immediately disappeared.

3rdly. By photography; employing concentrated solutions of quinine mixed with chloride of ammonium in troughs to intercept the incident light from any object anterior to the camera, when it was found almost impossible to obtain any image upon the sensitive collodion plate, although the intensity of the visible image received on the ground-glass screen did not suffer any apparent diminution.

4thly. By photographic printing; troughs containing these solutions obstructed the chemical rays very considerably, thus interfering with the production of a positive picture from the negative, much longer exposure being necessary to produce any chemical effect.

III. That certain reagents do not destroy fluorescence; others only mask its appearance by their own colour; whilst some destroy it by neutralizing the excess of acid; others do so by producing salts which are themselves non-fluorescent media. Whilst a third class destroy it by really modifying the alkaloid itself.

IV. That as so many reagents of common occurrence interfere with the manifestation of fluorescence, and as it is also a property common to all the cinchona alkaloids herein described, its appearance becomes no longer of any value as a test for quinine.

V. Brandes's chlorine and ammonia test will discover 1 grain of either quinine or quinidin in 1 gallon of water, but shows no difference between these alkaloids, except in very concentrated solutions, when there is a precipitate with quinidin, but not with quinine.

Quinicine is also influenced by this test, but less extensively.

VI. Dr. Vogel's first modification of this test is of no apparent value; but by also employing ammonia, the author has found that it will indicate both quinine and quinidin, detecting readily 1 grain of either in a pint, and showing slight evidence with 1 grain in 10,000 grains of water.

There is scarcely any reaction with quinicine.

VII. Dr. Vogel's other modifications of Brandes's test are unimportant, with the exception of the fourth, viz. excess of chlorine, and very little ammonia. This detects 1 grain in about 2000 grs. of fluid very readily, if excess of acid be avoided at first. The test,

however, is equally indicative of quinidin; it gives scarcely any perceptible reaction with quinicine.

VIII. Pelletier's chlorine gas-test succeeds very well with the free alkaloids, but does not show any indication with their salts. It is equally capable of detecting quinidin, and gives the same phenomena.

IX. Marchand's test is not a delicate reaction.

X. All the foregoing tests, although specially proposed for the discovery of quinine, possess equal powers and show the same appearances with quinidin. But they have no reaction on cinchonine, cinchonidin, or cinchonicine.

XI. Van Heijningen's test by oxalate of ammonia, produces, after some hours, a crystalline oxalate of quinine, when using a fluid containing only 1 grain of alkaloid in 800 grs. of water, and very readily detects immediately 1 part in 350. It does not precipitate quinidin or cinchonidin, but it produces a white precipitate in concentrated solutions of cinchonine.

XII. De Vry's test for quinidin by hydriodic acid, or iodide of potassium in neutral solutions, produces a well-marked crystalline precipitate as a colourless salt, when one part of the alkaloid is present in 1000 of the fluid; the crystals, being short hemihedral prisms, are readily recognized; the neutral hydriodates of cinchonidin are colourless, silky, prismatic needles, and much more soluble. If to a solution of the sulphate of quinidin in dilute spirit ($\frac{1}{3}$) we add hydriodic acid, and expose to the action of light during some days, there is formed the red iodo-sulphate of the author.

The neutral hydriodate of quinine appears as lemon-yellow prisms. The neutral hydriodate of cinchonine appears as long, thick, colourless prisms, and is very soluble.

XIII. Liebig's ether test dissolves quinine, quinicine, and cinchonicine, and therefore does not discriminate between them, as they are all uncrystallizable. It dissolves also a portion of the quinidin and cinchonidin. Should the proportions of these alkaloids not exceed the solvent powers of the ether employed, they will not be indicated by this test. When crystallization occurs, the rhombic prisms indicate cinchonidin; the long slender aciculæ, quinidin; whilst an amorphous powder is demonstrative of cinchonine. Ether also extracts cinchonidin from cinchonine; but its sparing solubility in ether necessitates the employment of warmth, and a large quantity of ether.

XIV. Leers' combination of the ether test with that of Brandes can readily detect small portions of quinine, quinidin, or quinicine in cinchonine or cinchonidin, especially when used in the manner as modified by the author.

PART II.—On the Optical and Chemical Characters of the Iodo-Sulphates of the Cinchona Alkaloids, Quinine, Quinidin and Quinicin, and Cinchonine, Cinchonidin and Cinchonicine; together with the Chemical Analysis of many of the Salts, and new methods of discriminating those Alkaloids, founded upon the production of these remarkable compounds, and the recognition of their optical characters.

In the former part of his paper, the author examined the existing tests for discriminating between the various cinchona alkaloids, and pointed out their insufficiency. In the present part, he shows that the optical characteristics of the iodo-sulphates of the alkaloids quinine and quinidin are sufficiently well marked to render the existence of *either one* of these alkaloids *certain*, and that although the iodo-sulphate of cinchonidin is very closely related optically and chemically to the homologous salt of quinine, yet there are sufficient points of dissimilarity to enable us to diagnose between the two; and, moreover, that the production of this salt is a beautiful means of deciding readily whether cinchonidin is present in specimens of cinchonine or cinchonicine; all evidence of quinine or its allies having been decided in the negative by the results of the previous tests, as proposed by Brandes, Vogel, Pelletier, Leers, or the author.

The cinchonidin of Wittstein has also, by the same method, been proved by the author to be totally different from the cinchonidin of Pasteur.

Acetic acid and chloroform may also be employed for discriminating between cinchonine and cinchonidin.

The *chemical characters* of all these iodo-salts furnish no means of discrimination, for as a class they all agree in being more or less soluble in spirit, giving a deep sherry-brown solution, from which water precipitates them in an amorphous form, as dark brown, cinnamon-brown or purplish-brown coloured precipitates; they are

only very slightly soluble in dilute spirit, and scarcely at all in water, ether, turpentine, or chloroform: acetic, dilute sulphuric, or hydrochloric acid have but little action upon them, whilst concentrated hydrochloric or sulphuric acid decomposes them. Nitric acid rapidly acts upon them, even in the cold, with violent evolution of nitrous acid and production of heat, iodine being oftentimes liberated in the crystalline form.

Alkalies also decompose them.

Sulphuretted hydrogen, soluble sulphides, sulphurous acid and sulphites, together with chlorine-water, instantly decolour their alcoholic solution, with the production of hydriodic acid.

In dilute alcoholic solutions, starch gives immediate evidence of iodine, and nitrate of silver gives a yellowish-white precipitate of iodide of silver, and some organic basic compound which can only be removed by the action of concentrated boiling nitric acid; this reaction, although commencing at the ordinary temperature, with violent disengagement of nitrous acid vapours, must be perfected by boiling.

Baryta salts exhibit the existence of sulphuric acid, which in all instances is an essential constituent in their formation.

The quinidin and cinchonine salts dissolve with more difficulty, in consequence of their greater thickness and less extent of surface.

Since the author had the honour of communicating his discovery of the optical salt of cinchonidin to the Royal Society (a preliminary notice of which was published in the 'Proceedings,' vol. viii. No. 24), he has ascertained that its primary form is, like that of the quinine salt, that of a right rhombic prism, and usually very thin, but having for its acute angles 43°, and 137° for its obtuse, with the rectangular axes $M^{a}_{2\cdot482}$; $T^{a}_{1\cdot000}$; $P^{a}_{\cdot00001}$—the quantity for P^{a} being variable and very minute. In a former communication to the Royal Society, published in the 'Proceedings' (Feb. 16, vol. vi. No. 24, 1854), the quinine salt was shown to have a primary rhombus, having 65° for the acute, and 115° for the obtuse angles, with the three rectangular axes, thus related:—$M^{a}_{1\cdot57}$; $T^{a}_{1\cdot000}$; $P^{a}_{\cdot00001}$.

In both salts the optical characters are usually examined through the shortest axis, P^{a}: in some recent observations on the quinine salt, the author has discovered that it transmits a *blood-red* beam of plane-polarized light through the axes M^{a} and T^{a}, and this is also a beam polarized in a plane parallel to that of the axes M^{a} and T^{a}.

TABULAR VIEW.

Both the quinine and cinchonidin salts are derivable from the primary rhombic prism, and crystallize as rhomboids and β-prisms . . . . . } which obstruct plane-polarized light, when their longer diameters (M^a) are parallel to the plane of the polarized ray.

and α-prisms } which obstruct the same beam when their longer diameters (T^a) are perpendicular to the plane of the polarized ray.

Quinine salt		Cinchonidin salt
Rhomb obtuse 115°		Rhomb 137°
„ acute 65°		„ 43°
	1·57 = M^a = 2·482	
	1·00 = T^a = 1·000	
	·00001 = P^a = ·00001	

Transmitted rays or body-colours.	1. *Polarized parallel to axis* (T^a). P^a, colourless, greenish-white, yellowish-green..	1. P^a, greenish-white, yellowish-green, dark olive-green.
	2. M^a and T^a, blood-red, *polarized in the plane of those axes*	2. M^a and T^a not observed.
	3. *Polarized perpendicular to axis* (T^a). P^a, pink, ruby-red, blood-red, sienna-brown ...	3. P^a, violet, light blue, indigo-blue.
Reflected rays or surface-colours.	1. *Polarized perpendicular to axis* (T^a). Cantharidin-green, blue-green, grass-green	1. Brassy-yellow, golden-yellow, orange.
	2. *Polarized parallel to axis* (T^a). Dull olive-green, or vitreous and colourless on a dull black surface.	2. Dull olive, or vitreous and colourless on a dull black surface.

In the foregoing comparative Chart of the physical properties of the two salts, the axis has been assumed to coincide with a line drawn through the short diagonal of the primary rhombic crystal, which will coincide with the long diameter of the α-prism, and the plane of the breadth of the β-prism, and is therefore the T^a of the three rectangular crystallographic axes.

It has been compiled from the observations of Professors Stokes and Haidinger and the author. It appears to form a complete optical description of the two salts, as far as they are at present known.

Whilst in both salts the *indicative body-colours*, or those due to the more absorbed pencils (3), are only to be seen in the thinnest crystals, it is evident that the reflected rays may be seen indifferently in crystals of all thicknesses; and the author is inclined to believe that the cinchonidin salt possesses even greater tourmaline absorbent powers upon ordinary light, inasmuch as much thinner plates are required in order to obtain the indicative body-colours,—perfect absorption, and therefore total obstruction, being more early arrived at than in the case of the quinine salt.

The author's more recent analyses of the cinchonidin salts have produced the following results :—

Sulphate of Iodo-Cinchonidin.

	I.	II.	III.	IV.	Mean.
Iodine.....	39·727	39·462	39·246	38·488	39·478
Sulph. acid..	8·390	8·673	8·882	8·593	8·701
Carbon	34·936	35·73	35·792	..	35·486
Hydrogen ..	4·321	4·301	..	..	4·311
Nitrogen....	2·976	..	..	..	2·976
Oxygen	9·650	..	..	..	9·048
	100·000				100·000

which lead to the following composition :—

					Theory.	Mean of Experiments.
57 Carbon	×	6	=	342	= 35·367	35·486
40 Hydrogen	×	1	=	40	= 4·147	4·311
2 Nitrogen	×	14	=	28	= 2·884	2·976
12 Oxygen	×	8	=	96	= 10·052	9·048
3 Iodine	×	127	=	381	= 39·297	39·478
2 Sulph. acid	×	40	=	80	= 8·294	8·701
				967	100·000	100·000

which probably give the following formula :—

$$\left.\begin{matrix} C^{57}\,H^{33}\,N^{2}\,O^{5} \\ I^{3} \end{matrix}\right\} 2SO^{3},\,HO+5HO=967.$$

One other remarkable difference exists between the quinine and cinchonidin salt, which is, that the optical crystals of the last salt, if allowed to remain in the mother-solution with an excess of less than 1 per cent. of sulphuric acid, undergo a transformation, and become long, golden, silky aciculæ, radiating in beautiful globose tufts : this salt has some doubly absorbent powers also, but very feeble. When this salt is attempted to be redissolved in boiling spirit, in order to be recrystallized, it does not re-form, but the optical crystals are then produced ; when the silky crystals are carefully air-dried, they retain their yellow colour, but if exposed over sulphuric acid at 62° Fahr., or if attempted to be dried at 212° Fahr., they lose 5·32 per cent. water = 6 atoms, and become a dark greenish-black residue, which is a tri-hydrate and contains the following by analysis :—

	I.	II.	III.	IV.
Iodine	40·504	40·407	..	..
Sulph. acid....	9·064	8·324	..	..
Carbon	..	..	36·082	35·689
Hydrogen	..	36·404	36·28	36·583

numbers which very closely correspond with the following :—

				Theory.	Experiment.
57 Carbon	× 6	= 342	=	36·037	35·835
38 Hydrogen	× 1	= 38	=	4·004	4·047
2 Nitrogen	× 14	= 28	=	2·950	2·851
10 Oxygen	× 8	= 80	=	8·433	8·063
3 Iodine	× 127	= 381	=	40·147	40·455
2 Sulph. acid	× 40	= 80	=	8·429	8·699
		949		100·000	100·000

and the formula may be provisionally given as—

$$\left.\begin{matrix} C^{57}\,H^{33}\,N^{2}\,O^{5} \\ I^{3} \end{matrix}\right\} 2SO^{3},\,HO+3HO=949,$$

which closely corresponds with the optical salt, but contains 2 atoms less water.

If this olive-coloured residue be boiled in dilute spirit, the optical crystals deposit on cooling.

From the addition of 5·32 per cent. water to this dry residue, we find that the silky crystals contain dry residue,—

	94·678 = 949	= 1 atom
Water	5·322 = 54	= 6 atoms
	100·000 1003	

and we have thus the following formula for the silky salt, which corresponds most closely with the result of analysis,—

$$\left.\begin{matrix} C^{57}\,H^{33}\,N^{2}\,O^{5} \\ I^{3} \end{matrix}\right\} 2SO^{3}\,HO + 9HO = 1003,$$

as may be seen by the following comparison:—

				Theory.	Experiment.
57 Carbon	× 6	= 342	=	34·097	33·947
44 Hydrogen	× 1	= 44	=	4·386	4·423
2 Nitrogen	× 14	= 28	=	2·791	2·700
16 Oxygen	× 8	= 128	=	12·764	12·800
3 Iodine	× 127	= 381	=	37·986	37·914
2 Sulph. acid	× 40	= 80	=	7·976	8·216
		1003		100·000	100·000

giving—

Carbonic acid.....	125·22	124·472 per cent.
Water.....	39·474	39·807 ,,

Consequently the silky salt will be the optical salt + 4 atoms of water, which, under the influence of excess of sulphuric acid and prolonged delay at 62° Fahr., are assimilated by that salt; and which additional water, on boiling in spirit, is lost, and the optical salt recrystallized on cooling.

If the temperature be not too high *at first*, the silky crystals may be produced without the appearance of the optical. And the silky crystals at 212°, or at 62° Fahr. over sulphuric acid, become the dry residue or tri-hydrate, which, when boiled in spirit, becomes the optical, by assimilating 2 atoms of water, as may be seen by comparing the three proposed formulæ:—

a. Optical.

$$\left.\begin{matrix} C^{57}\,H^{33}\,N^{2}\,O^{5} \\ I^{3} \end{matrix}\right\} 2SO^{3}\,HO + 5HO = 967$$

β. Silky Salt.

$$\left.\begin{matrix} C^{57}\,H^{33}\,N^{2}\,O^{5} \\ I^{3} \end{matrix}\right\} 2SO^{3}\,HO + 9HO = 1003.$$

γ. Dry Residue.

$$\left.\begin{matrix} C^{57}\,H^{33}\,N^{2}\,O^{5} \\ I^{3} \end{matrix}\right\} 2SO^{3}\,HO + 3HO = 949.$$

The results of the analysis of the cinchonidin salt having been so remarkably different from those of the formulæ generally adopted for the pure alkaloid, the author was induced to prepare some perfectly pure quinine, taking especial pains to exclude all cinchonidin; and having from that prepared some iodo-sulphate of quinine, to submit it to equally rigid analysis.

The results are the following:—

These optical crystals lose 2·49 per cent. water by prolonged drying at 212° in Liebig's drying apparatus.

The residue contains the following:—

	I.	II.	III.	IV.	V.
Iodine	30·195	30·033	30·50	31·729	31·69
Sulph. acid	10·246	9·352	..	9·631	9·854
Carbon	41·554	..	41·34	41·456	41·048
Hydrogen	4·766	4·762	..	4·54	4·7375
Nitrogen	3·711	..	..	3·380	..

Carbonic acid mean of 4 = 151·614
Water ..... = 42·326

leading to the following composition:—

		Theory.	Experimental means.
57 Carbon	= 342	= 41·606	41·3496
38 Hydrogen	= 38	= 4·623	4·7025
2 Nitrogen	= 28	= 3·409	3·5455
10 Oxygen	= 80	= 9·730	9·8024
2 Iodine	= 254	= 30·900	30·8925
2 Sulph. acid	= 80	= 9·732	9·7705
	822	100·000	100·000

which, with 2 atoms water, constitute the optical salt dried over sulphuric acid at 62° Fahr., thus :—

1 atom dry residue	822
2 atoms water	18
	840

and these results may be expressed by the following formula :—

$$\left.\begin{matrix} C^{57}\,H^{33}\,N^{2}\,O^{5} \\ I^{2} \end{matrix}\right\} 2SO^{3}\,HO + 5HO = 840,$$

which appears to be the constitution of the optical salt dried at 62° Fahr. over sulphuric acid.

From this it appears that the optical salt of quinine differs in chemical atomic numbers merely in the possession of 1 atom less iodine, the cinchonidin salt having 3, the quinine salt 2 atoms iodine ; but in each case 2 atoms of sulphuric acid, and 5 water, with an organic base of $C^{57}\,H^{33}\,N^{2}\,O^{5}$ common to both. How this is derived from $C^{40}\,H^{24}\,N^{2}\,O^{4}$ in the one case, or $C^{40}\,H^{24}\,N^{2}\,O^{2}$ in the other, it is difficult to point out in the present state of the question.

Were these views correct, it might naturally be imagined that the two salts may be mutually convertible. The author has undertaken numerous experiments with this object in view ; and whilst he has proved that it is possible (by boiling the quinine salt in spirit surcharged with iodine) to communicate the golden tint of the reflected ray and the blue tint of the body-colour to the crystals on their re-formation, yet this modified salt retains the crystallographic forms of the true quinine salt ; whilst, by treating the cinchonidin salt by spirit and aqueous sulphurous acid, that salt is modified also, becomes fibrous in character, and assumes the red body-colour of quinine salt, yet is at once to be distinguished from the true quinine salt even by the naked eye alone ; and on redissolving these in spirit, the blue body-coloured salt again recrystallizes with its ordinary golden reflected tint. The effect of diluted sulphuric acid in converting the cinchonidin salt into the golden silky fibrous variety, is a striking distinguishing characteristic between the two alkaloids.

These facts lead to the conclusion, that the grouping of the constituent molecules in the two salts differs materially ; that closely as the quinine and cinchonidin salts agree amongst themselves, they differ widely from the quinidin and cinchonine compounds.

The quinidin salt, after recrystallization, presents itself as long

quadrilateral acicular prisms, having a deep ruby or garnet-red colour, with a bluish-violet or light purplish reflexion-tint; it is sometimes deposited in thin flat plates, or long, flat, acicular prisms; these, when thin, transmit a pure yellow colour, but in thicker plates it becomes reddish, with a tinge of brown.

There is scarcely any appearance of double absorption in this salt; the thicker crystals alone exhibit it, when their usual tint becomes darkened on analysis with a Nichol.

This salt requires 31 parts of boiling spirit, and 121 parts at 62° to dissolve 1; water precipitates it as a cinnamon-brown powder.

Its deep marone-coloured large aciculæ had a specific gravity of 1·7647 at 62°.

These large crystals, exposed whole to a temperature of 212°, decrepitate afterwards on exposure to the air, but dried at 212°, they do not appear to lose further water after prolonged exposure to the drying bath.

The author having supplied Dr. Sheridan Muspratt with a quantity of this salt, has been most obligingly furnished with the results of his examination; from which it will be seen that those previously obtained by the author have been confirmed in the most satisfactory manner by that experienced analyst.

	Herapath.				Muspratt.	
	I.	II.	III.	IV.	I.	II.
Iodine.....	39·665	39·570	39·740	39·88	39·73	39·131
Sulph. acid..	6·273	6·390	6·326	6·302	6·263	..
Carbon	32·890	32·615	32·787	..	31·998	32·311
Hydrogen ..	3·960	3·958	4·028	3·985	4·001	3·937
Nitrogen....	4·400	4·440	4·440			
Oxygen	12·812	13·027	12·697			
	100·000	100·000	100·000			

The formulæ derivable from these analyses are the following:—

					Theory.	Herapath.	Muspratt.
35 Carbon	×	6	= 210	=	32·967	32·764	32·154
25 Hydrogen	×	1	= 25	=	3·924	3·984	3·969
2 Nitrogen	×	14	= 28	=	4·395	4·44	..
10 Oxygen	×	8	= 80	=	12·559	12·743	..
2 Iodine	×	127	= 254	=	39·874	39·73	39·78
1 Sulph. acid	×		40	=	6·274	6·339	6·263
			637		100·000	100·000	

and give—

$$\left.\begin{matrix} C^{35}\,H^{19}\,N^{2}\,O^{4} \\ I^{2} \end{matrix}\right\} 1SO^{3}\,HO + 5HO = 637,$$

which differs from Gerhardt's formula for quinidin by the loss of $C^{5}\,H^{5}$; but at this stage of the question it is scarcely possible to arrive at a solution of the manner in which it is produced.

The cinchonine salt differs much from all those previously described; it exists in long, acicular, quadrilateral prisms, of a deep purplish-black colour, like that of elder-berries.

Thin crystals transmit a yellow tint—pure gamboge-yellow when very thin; soon passing through a deep sherry-brown to a blood-red colour, then a deep port-wine colour, and then becoming opaque.

These crystals reflect a deep steel-blue colour when analysed with a Nichol's prism, and generally across the short diameter of the prism, which is the analogue of the α-prism of the quinine salt. The cinchonine salt possesses doubly absorbent powers, much more powerfully so than the quinidin salt, but inferior to all the others; the body-colour is deep sienna or bistre-brown.

This salt furnished the following analytical results:—

	I.	II.	III.
Iodine	50·34	50·587	50·302
Sulphuric acid ..	5·247	5·217	..
Carbon	28·156	27·57	27·37
Hydrogen	3·523	3·485	3·454
Nitrogen	3·306	..	..

which lead to the following composition:—

					Theory.	Experiment.
35 Carbon	× 6	=	210	=	27·7410	27·698
26 Hydrogen	× 1	=	26	=	3·4346	3·487
2 Nitrogen	× 14	=	28	=	3·7000	3·306
9 Oxygen	× 8	=	72	=	9·5103	9·8674
3 Iodine	× 127	=	381	=	50·3301	50·4096
1 Sulph. acid		=	40	=	5·2840	5·232
			757		100·000	100·000

giving—

$$\left.\begin{matrix} C^{35}\,H^{19}\,N^{2}\,O^{2} \\ I^{3} \end{matrix}\right\} 1SO^{3}\,HO + 6HO = 757,$$

which, on comparison with the quinidin salt, will be found to possess 1 atom additional iodine, and 1 atom more water, but a deficiency of 2 atoms oxygen, the latter, apparently, in consequence of the original difference in the type of the alkaloids employed; and, like that salt, it differs in its organic base by the loss of $C^5 H^5$ from the constitution of the alkaloid originally employed, if we take the formula $C^{40} H^{24} N^2 O^2$, as given by Gerhardt, for that of cinchonine.

The cinchonine and quinidin salts further agree in containing only 1 atom sulphuric acid, whereas the quinine and cinchonidin salts contain 2 atoms.

These investigations appear to show that the alkaloids in each instance undergo some modification, but not analogous to substitution; it appears more like a splitting-up into different molecular groups, and a rearrangement of these amongst themselves, as the formulæ of the organic bases differ much from those of the original alkaloids.

All these iodo-salts possess double refractive properties.

When the acid sulphates of the mixed alkaloids, quinine, quinidin, cinchonine and cinchonidin, are dissolved in dilute spirit, and the temperature increased to 80° or 120°, treatment with tincture of iodine readily separates the quinine salt first.

Subsequent further treatment in the same manner produces the cinchonidin salt, more or less mixed with the quinine salt.

On still further treatment, the quinidin salt is formed with its well-marked characters.

The cinchonine salt is by far the most soluble in spirit; and when a large quantity of cinchonine exists, this compound will also appear along with the quinidin salt.

This test is a beautiful and ready method of proving the presence of cinchonidin in cinchonine, which would otherwise be considered pure, Brandes' test having shown the absence of quinine and quinidin. In the same way, this test is an easy method of detecting mixtures of quinine and quinidin, the optical characters of the two salts being so well marked, that no difficulties can exist in their discrimination.

It does not offer such facilities for the separation of quinine from cinchonidin; the two salts go down together, especially if large quantities of cinchonidin exist with mere traces of quinine.

For the success of this test, a small portion only is necessary: with quinine and quinidin $\frac{1}{200}$th part of a grain has furnished evidence of the two alkaloids; one grain would be abundant to detect all the alkaloids.

The foregoing method of examination has enabled the author to prove that the substance which Rosengarten, of Philadelphia, called quinidin, was really the cinchonidin of Pasteur, and the details of his cures of fever, therefore, by quinidin are rather to be ascribed to cinchonidin.

The cinchonidin of Wittstein, of Munich, is a totally different alkaloid, giving, with sulphuric acid and iodine, a salt at once to be distinguished by the eye from either of the two iodo-sulphates described, but yet possessing optically doubly absorbent powers. This salt has a deep orange-yellow colour by transmitted light, merging into sienna-brown in thicker plates, which are generally flat and much imbricated in the method of crystallization, and also derived from a rhombic prism. The reflected tints are brownish-olive, not unlike dead leaves, or brown beech-leaves. These crystals are more doubly absorbent than either the quinidin or cinchonine salt, but less powerfully optical as tourmalines than the quinine or cinchonidin compounds. When polarized, they transmit a sienna-brown body-colour if moderately thick, and thicker plates are bistre-brown, but when sufficiently thick, they are wholly impervious to plane-polarized light. The substance was not in sufficient quantity to admit of any analysis.

All the alkaloids were furnished in a most obliging manner by Mr. John Elliott Howard, to whom the author is deeply indebted for them, and thus publicly desires to express his acknowledgments; many of these various alkaloids having taken more than ordinary trouble in the preparation and purification.

It is well known that quinine and quinidin, under the continued effect of heat and dilute sulphuric acid, undergo a molecular change into quinicine, which M. Pasteur has asserted to be isomeric with the original alkaloids, but hitherto no complete analysis has been made of the metamorphosed alkaloids.

The author has produced an iodo-sulphate of quinicine, but it is no longer a crystalline compound; it presents itself as a deep blood-coloured resin, very soluble in spirit and readily precipitated by water

from its spirituous solution. This substance has not yet been submitted to analysis. During the production of the iodo-sulphate of quinidin a certain portion of the alkaloid becomes converted into quinicine, as may be demonstrated by the production of this resinous compound from the mother-liquid on the addition of further proportions of iodine.

Cinchonine and cinchonidin become converted into cinchonicine by similar treatment, and this amorphous uncrystalline alkaloid also forms a resinous iodo-sulphate; its colour is deep purple-black, and it deposits itself on spontaneous evaporation of the spirit, or on the cooling of a highly concentrated spirituous solution, in small drops, highly tenacious at 100° Fahr., but becoming solid at 60° Fahr. This compound has, in a fine state of division, a beautiful purplish-blue colour, and such a film generally forms around the edge of the vessel in which it is produced.

Cinchonicine appears to be one of the products during the manufacture of the iodo-sulphate of cinchonidin, but there is a much larger production of it during the formation of the cinchonine salt.

From the foregoing reactions, the author appears to be justified in asserting that eventually it will be found, when we know more of the rational grouping of the constituent atoms of the vegeto-alkaloids, that the construction of the formula for the cinchonidin of Pasteur will have a much greater similarity to the arrangement of the molecular groups of quinine than of cinchonine. And there is also great probability that the grouping of the atoms of cinchonine and the quinidin of Pasteur will be found to present more points of similarity; but in each case he sees no reason to doubt the existence of more oxygen in the cases of both quinine and quinidin than there is in cinchonine and cinchonidin. He also ventures to suspect that cinchonicine and quinicine will eventually be found to contain more carbon than the original alkaloid, the elements of water probably being separated by the sulphuric acid during the process of formation.